Mechanistic Investigation for the Rechargeable Li-Sulfur Batteries

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Overview

Timeline

- Start: 10/01/2019
- Finish: 09/30/2020
- Percentage Complete:50%

Budget

- Funding received in FY19/20: DOE: $300k

Barriers addressed

- Alternative Li containing anode design to mitigate "shuttle effect".
- Li-S batteries with long calendar and cycle life.
- Polymer sulfur cathode material to mitigate polysulfide migration issues.

Collaborators

- Johnson Controls Inc.
- University of Washington Seattle.
- Pacific Northwest National Laboratory (PNNL)
- Argonne National Laboratory (ANL).
- University of Arkansas

- Department of Chemistry, Wuhan University.
- Department of Chemistry, Wuhan University of Science and Technology.
- Institute of Physics, Chinese Academy of Sciences

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Relevance and Project Objectives

- ***Overall Objectives***
  - ✓*Improvement of sulfur cathode performance based on the understanding of the detail mechanism of the sulfur redox reaction.*
  - ✓*Exploration of alternative Li containing anode to mitigate "shuttle effect" and development of long cycle life, high capacity Li-S batteries.*

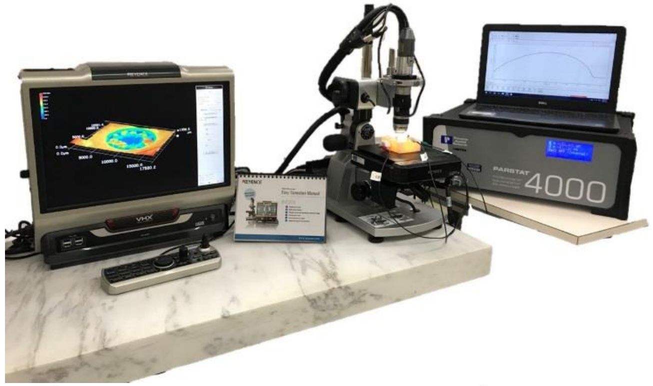
- ***Objectives this period: <u>to enable high energy, high cycle life Li-S batteries through mechanistic investigation and material engineering.</u>***
  - ✓*Synthesize cross-linked polymerized sulfur compounds, in which sulfur is attached to the conductive backbone with covalent bonds, therefore the polysulfides can be localized within the conductive matrix.*
  - ✓*Synthesize composite material with inorganic anchors for the localization of polysulfides*
  - ✓*Explore additives which can rapidly catalyze polysulfide radicals.*
  - ✓*Continue exploring the alternative anode materials which can cycle well and do not react with dissolved polysulfide and sulfur in the electrolyte, so "shuttle effect" can be mitigated.*
  - ✓*Develop in-site synchrotronic method to investigate the sulfur and polysulfide in the solid phase.*

Milestones

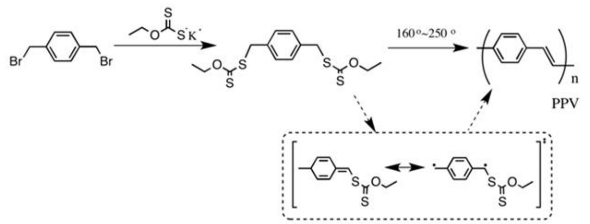
Milestone Name/Description	End Date	Status
Complete testing the newly synthesized polymeric sulfur compounds; Complete spatially resolved x-ray fluorescence (XRF) image and S-K edge x-ray absorption (XAS, including XANES and XAFS) studies of polymeric sulfur compounds.	12/31/2019	Completed
Complete survey alternative anode materials and determine their interaction with dissolved polysulfide ions; Continue synthesis and testing polymeric sulfur compounds and optimize the electrode making processes.	3/31/2020	Completed
Complete the investigation of radical disproportionation catalyst and test alternative electrolytes in which the solubility of polysulfide ions is lower than ether based electrolyte.	6/30/2020	On schedule
Complete the initial design of the full cell consisting of polymeric sulfur compounds, alternative anode and adequate additive in either coin cell or pouch cell format.	9/30/2020	On schedule

Approaches

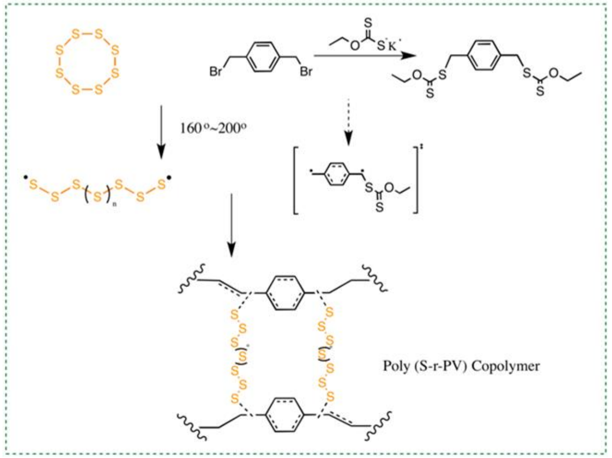
- *In-situ* ***High Performance Liquid Chromatography (HPLC)/Mass Spectroscopy(MS)-Electrochemical method.*** The overall electrochemical and chemical reactions of dissolved polysulfides can be monitored real time.
- *Ex-situ* X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to investigate the surface of sulfur cathode and Li anode to elucidate the surface changes during the Li-S battery operation’
- *In-situ* 3D microscope and electrochemical measurement in a specially designed cell to detect dendrite growth during cell operation.
- *In-site* synchrotronic method to investigation sulfur in solid state.
- Synthesis of polymer sulfur composite material to limit the dissolved polysulfide ion migration.
- Alternative Li containing anode.
- Extended collaboration with other US and international academic institutions and US industrial partners.



PPV Polymerization through the Xanthate Route: Diradical Character



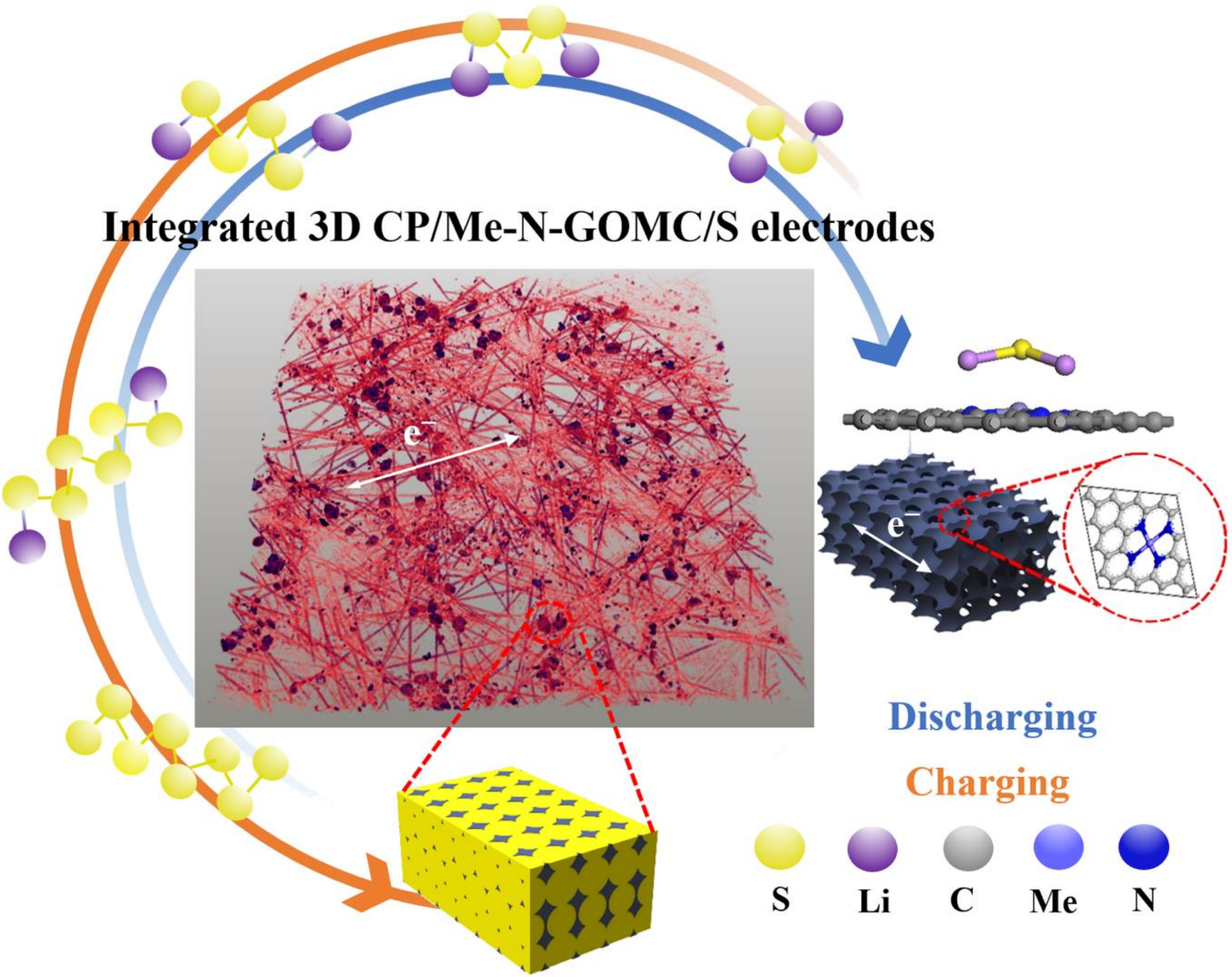
Polysulfur-*random*-PPV Copolymerizataion



Technical Accomplishments and Progress

- Li-S redox reaction mechanism became better understood through *in-situ* electrochemical MS studies.
- Synthesized various polymeric sulfur compounds and sulfur composite materials with inorganic anchors, with high rate and good cycle performance. The hypothesis that the strong chemical bonding in the matrix can limit the dissolution of polysulfide ions in the electrolyte has been proven. Thus, the “shuttle-effect” was reduced.
- Alternative Li-containing anode materials can significantly reduce the chemical interaction between the anode and dissolved polysulfide ions, which also can reduce the “shuttle-effect”.
- Synchrotron-based spectroscopic and microscopic studies reveal that sulfur is bonded to carbon in the polymeric sulfur and the sulfur distribution is generally uniform on the electrode.

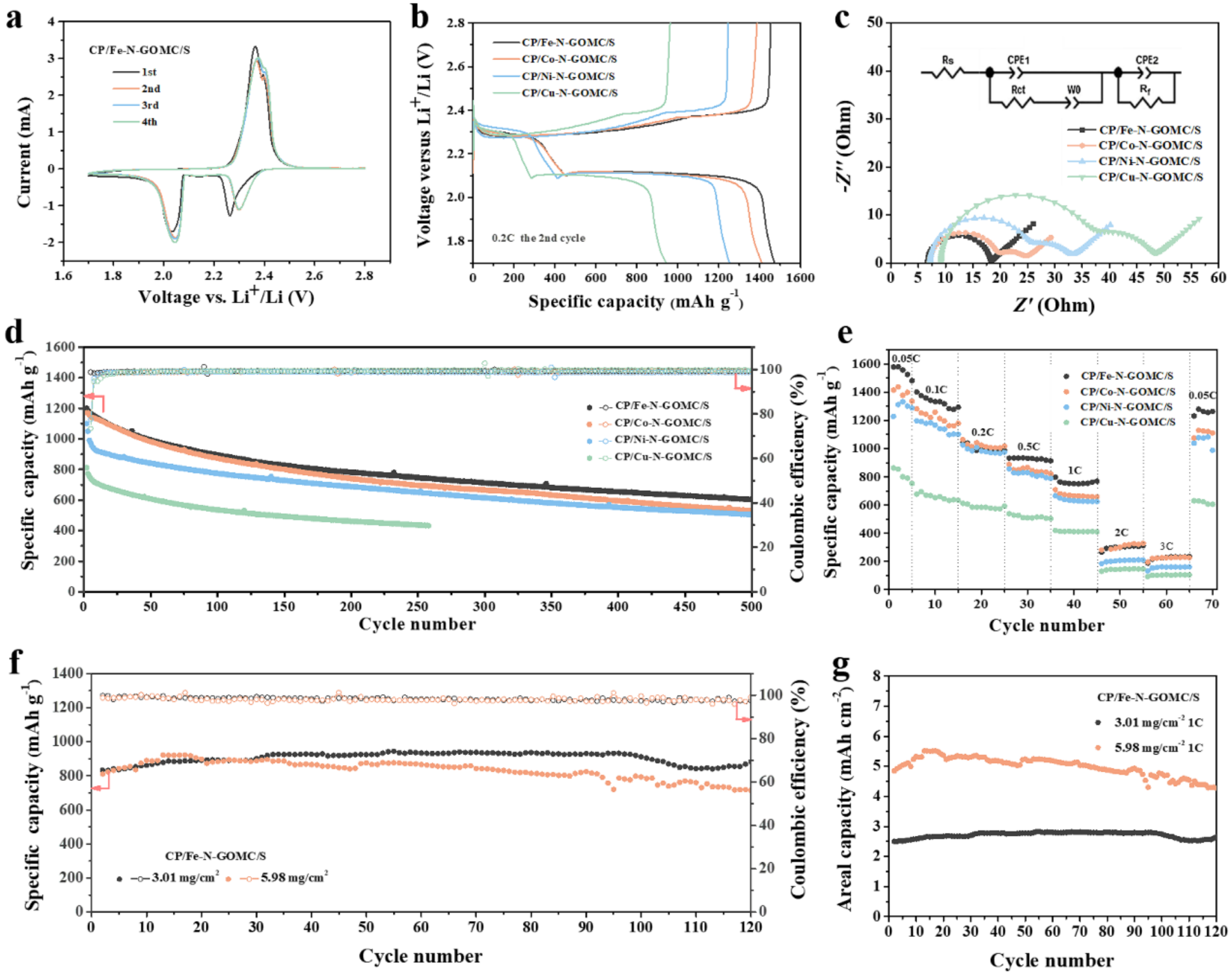
Example of Sulfur Cathode Architecture Engineering: Confinements of Polysulfides



Semi-graphitic ordered mesoporous carbons with metal/nitrogen doping (Fe, Co, Ni, and Cu anchors) are designed as sulfur hosts with abundant porosity and high electrical conductivity. It is revealed that the carbon capability of anchoring polysulfides can be remarkably enhanced through the synergistic effect of Fe and N doping.

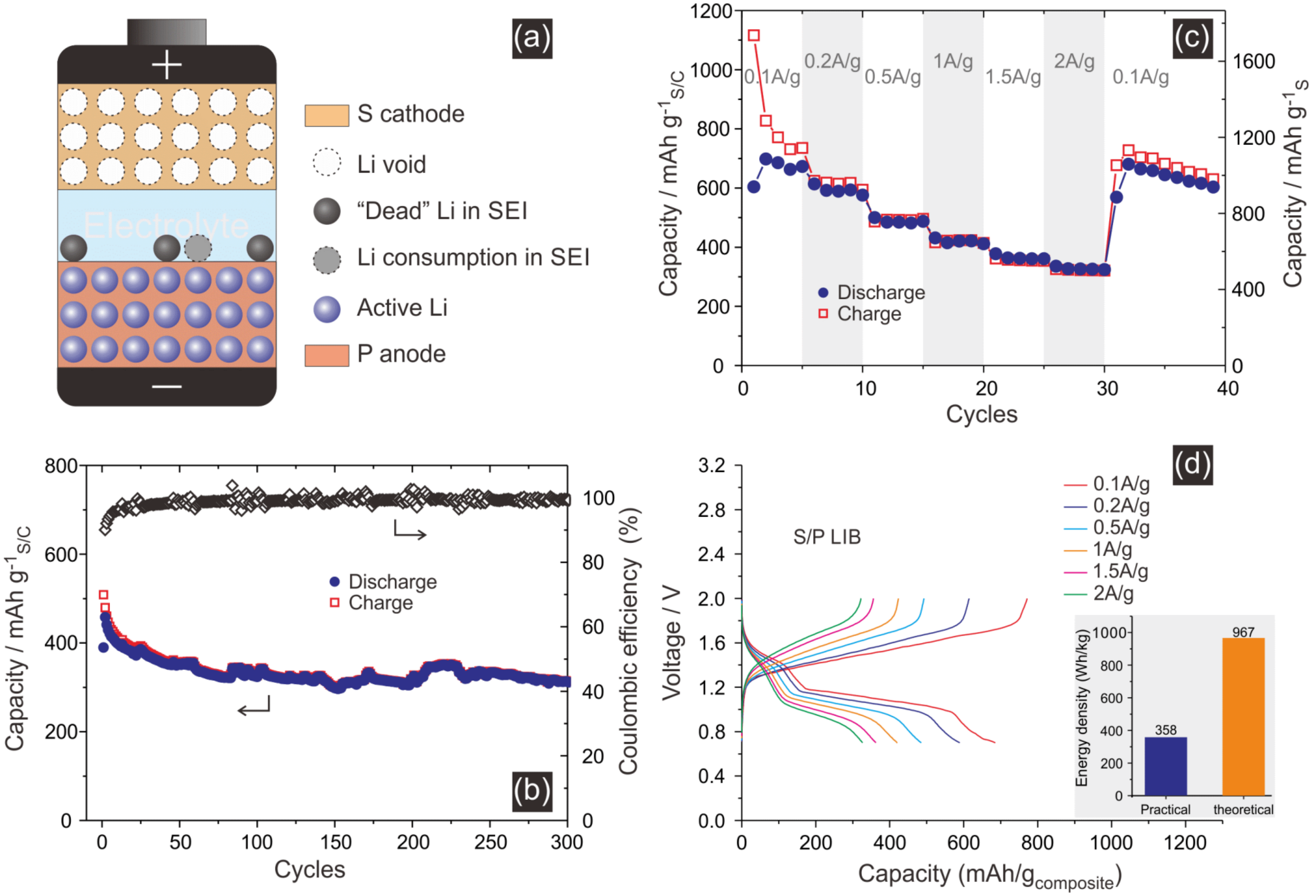
Example of Sulfur Cathode Architecture Engineering:

High Sulfur Loading (3 and 6 mg cm^{-2}), High Capacity (3 and 5 mAh cm^{-2}) and long cycle life



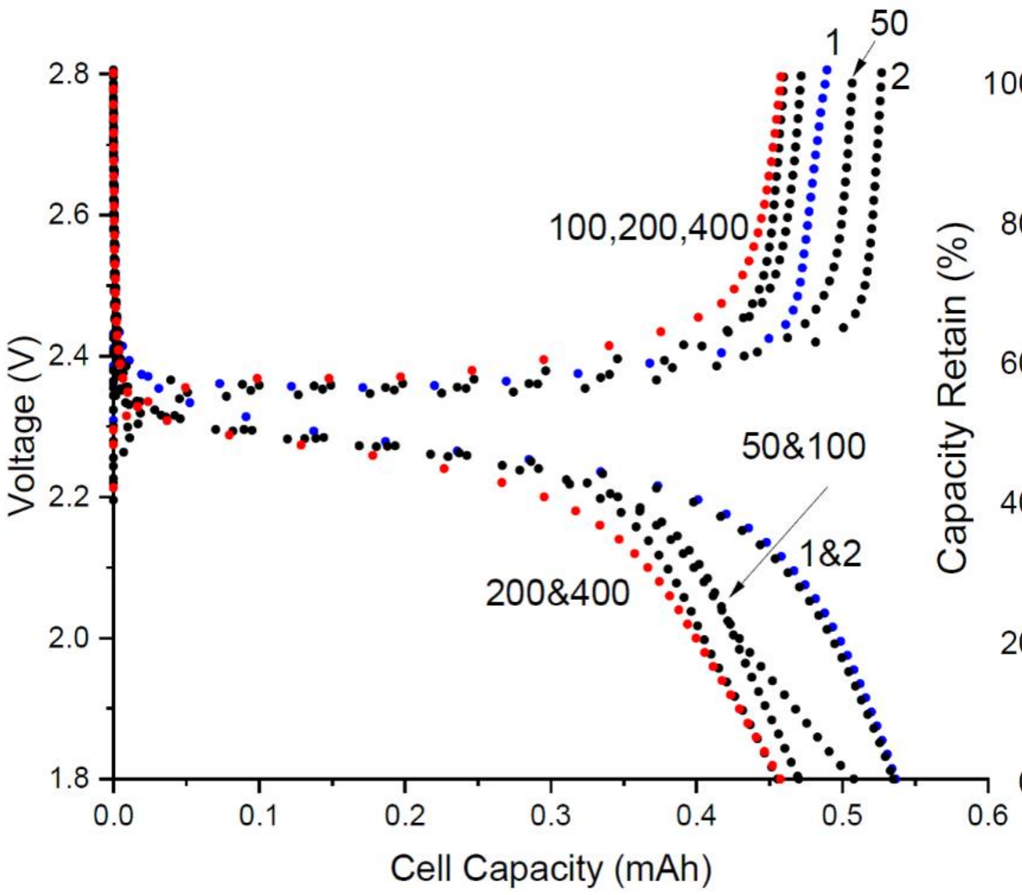
(a) CV curves of the Fe doped S cathode at 0.05 mV s^{-1}. (b) Discharge-charge profiles of electrodes (Fe, Co, Ni, Cu doped) at 0.2 C. (c) Nyquist plots of electrodes (Fe, Co, Ni, Cu doped) after initial cycle. (d) Cycling performances of electrodes (Fe, Co, Ni, Cu doped) at 0.5 C and (e) rate capability of electrodes (Fe, Co, Ni, Cu doped) with a sulfur loading of ~3 mg cm^{-2}. (f) Cycling performances of Fe doped S cathode with 3 and 6 mg cm^{-2} sulfur loading at 1 C and (g) the corresponding areal capacities.

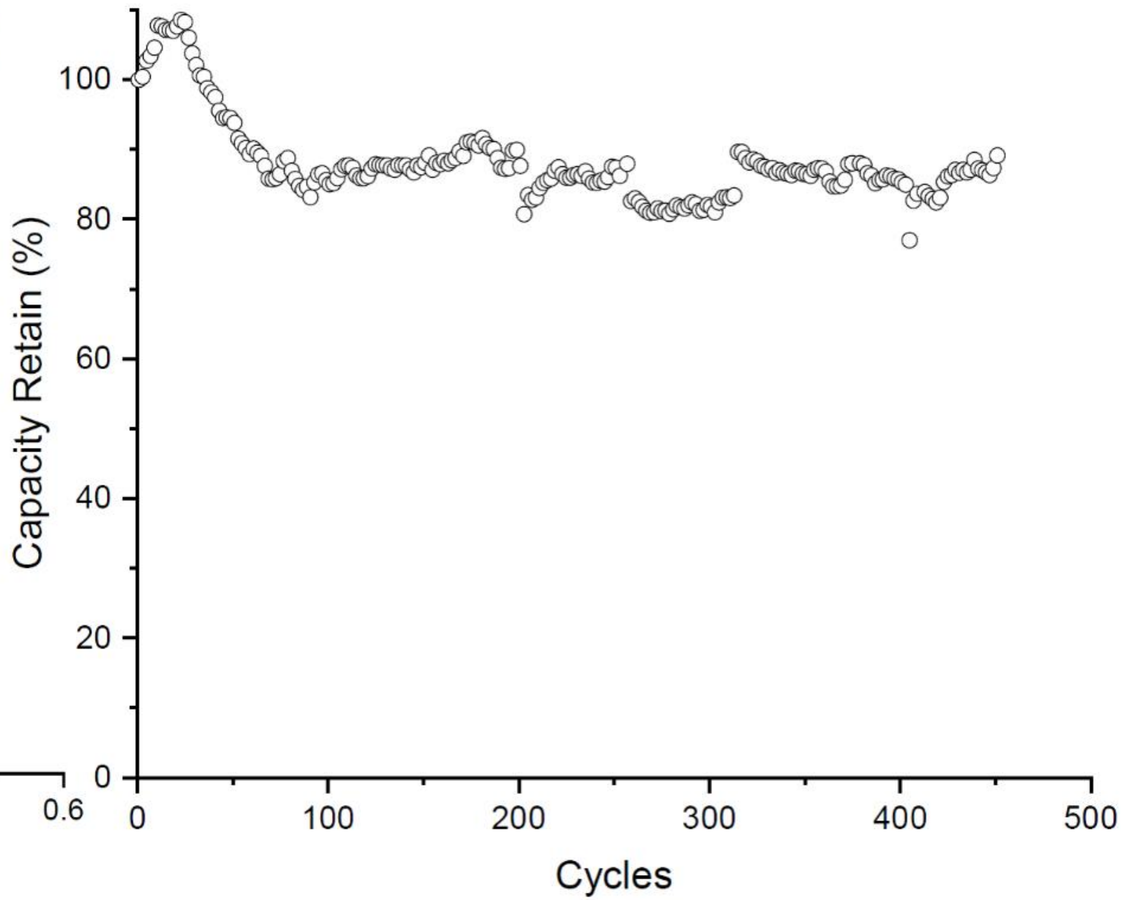
Example of Alternative Li Containing Anode: Pre-lithiated Phosphorus anode



Schematic illustration of the S/P LIB (a). Cycling performance of the S/P LIB at 1 A g-1S/C (b). Rate performance of the S/P LIB (c). Typical voltage profiles at different current densities (d). Insert is the theoretical and practical energy densities of the S/P LIB.

Synthesis and Test Polymeric Sulfur Materials: an example

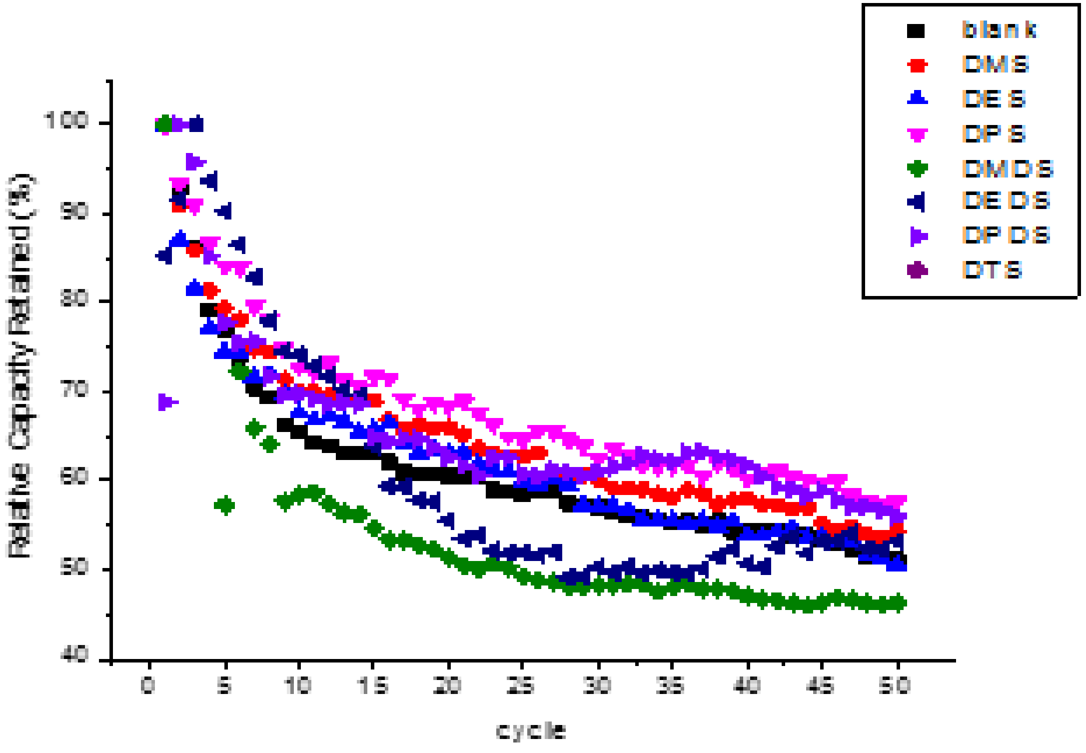




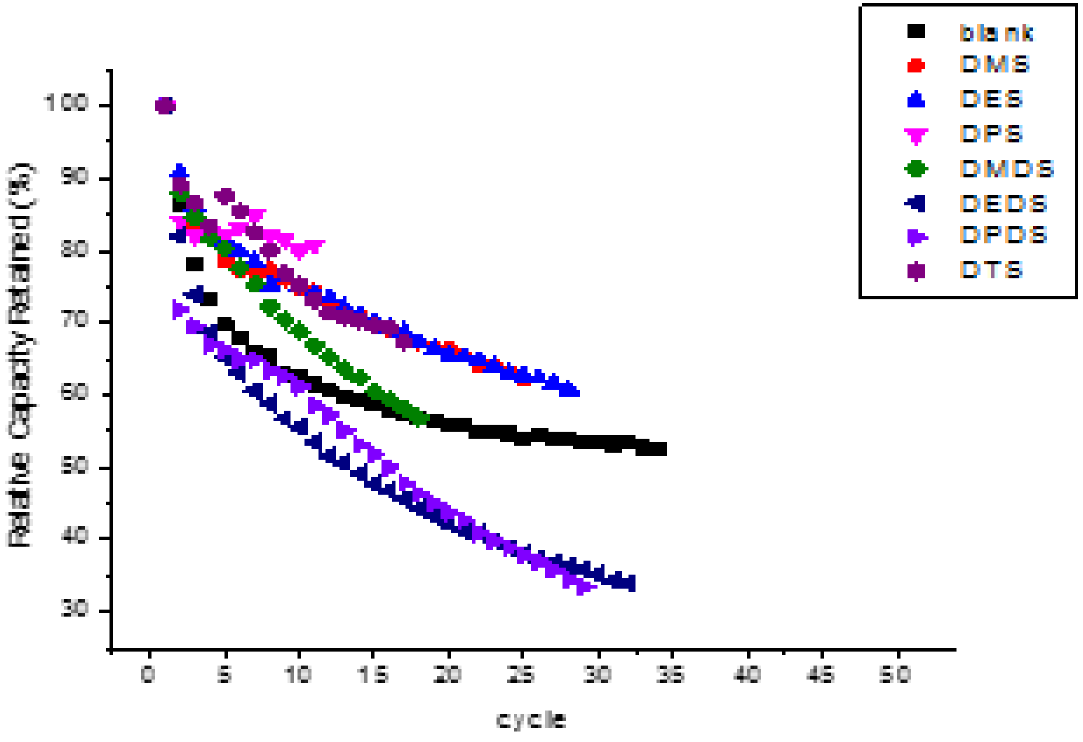
The charge and discharge curves of a polymeric S cathode (left); cycle life (right)

Evaluation and Testing Electrolyte Additives in Li/S Cells

- Seven small organic sulfides were investigated: CH3SCH3, C2H5SC2H5, C3H7SC3H7 (mono-sulfide), CH3SSCH3, C2H5SSC2H5, C3H7SSC3H7 (di-sulfide) and CH3SSSCH3 (tri-sulfide).
- Two types of sulfur cathodes were tested: a typical elemental sulfur cathode (prepared by infusing elemental sulfur S_8 into carbon matrix at 170◦C) was tested as a control; a polymeric sulfur cathode (prepared by polymerizing sulfur and monomer organic substrate under heated condition) was also tested

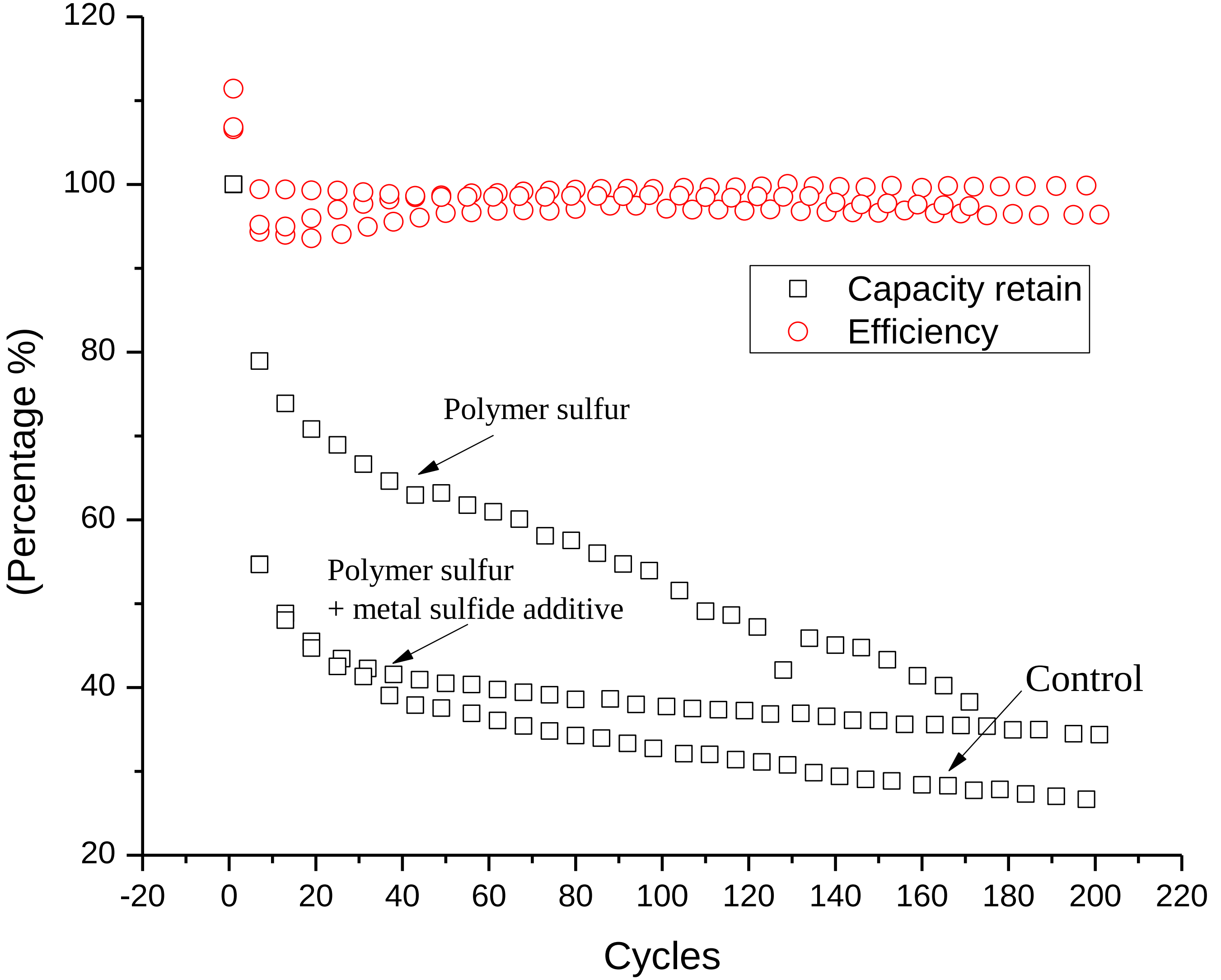


Polymeric Sulfur Electrodes



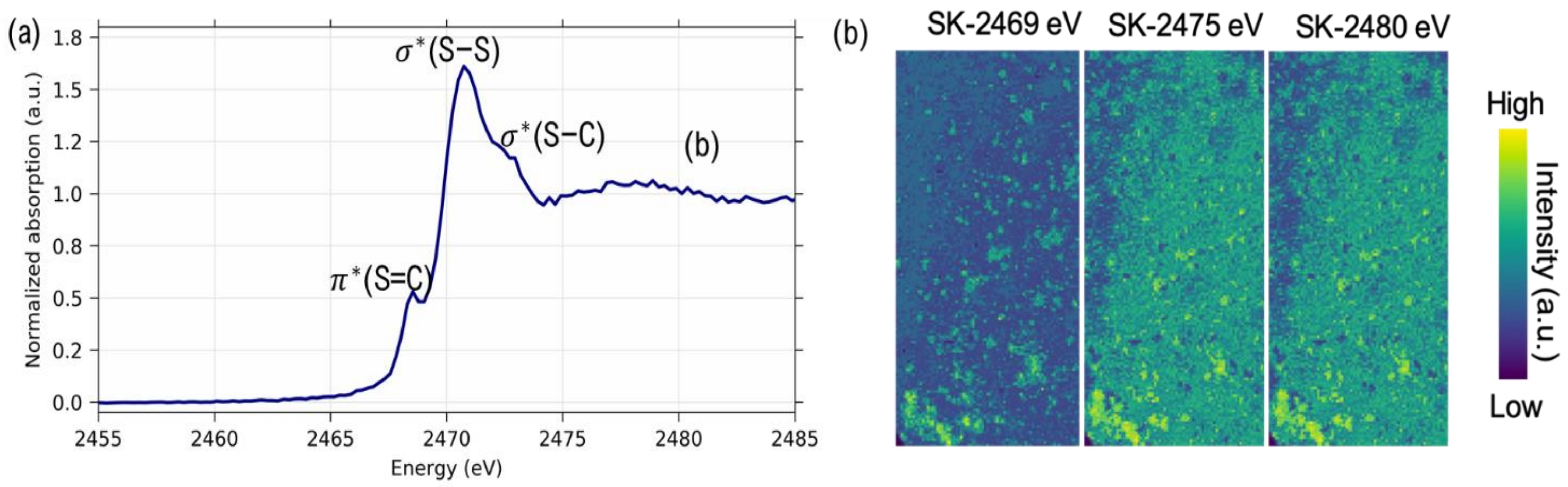
Regular Sulfur Electrodes

Evaluation and Testing Electrolyte Additives in Li/S Cells



The polymeric sulfur cathode without additive, the capacity kept decreasing throughout the whole duration of cycling, even though the initial capacity retention was better. The capacity decay of a polymeric sulfur cathode with an additive was mainly observed at beginning. After the 50th cycle, however, the capacity remained relatively steady. The mechanisms of such improvements are still under investigation.

XAS and XRF of pristine material



(a) XAS of pristine polymeric sulfur. Major peaks corresponding to characteristic unoccupied molecular orbitals are labelled. (b) XRF of pristine polymeric sulfur collected at energies of 2469 eV, 2475 eV, and 2480 eV.

Response to last year reviewer's comments

The Project was not reviewed in FY 2018

Collaborations with other institutions and companies

- **Johnson Controls Inc.**
  Optimization of sulfur cathode fabrication.
- **University of Washington Seattle**
  Solid state synthesis of sulfur cathode materials.
- **University of Arkansas**
  Material synthesis and sulfur loading.
- **Pacific Northwest National Laboratory (PNNL).**
- **Argonne National Laboratory (ANL)**
  Sulfur loaded carbon cloth electrodes

- **Department of Chemistry, Wuhan University**
  In situ electrochemistry – spectroscopy technique development.
- **Department of Chemistry, Wuhan University of Science and Technology**
  Synthesis of nano particle size sulfur materials
- **Institute of Physics, Chinese Academy of Sciences**
  Electrode structure analysis

Remaining Challenges and Barriers

- **It remains a challenge to optimize effective electrolyte and alternative anode materials which has high energy density while can prevent continuous reaction between polysulfide, sulfur and Li anode.**
- **The lack of adequate additives better than nitrate to prevent the "shuttle effect".**
- **To limit the diffusivity of dissolved sulfur and polysulfide ions beyond the surface coating and encapsulation, sulfur containing copolymer and inorganic anchors have been proven effective. Synthesis right structure copolymer which is cost effective and easy for electrode fabrication.**
- **Sulfur containing electrode with high sulfur loading and long cycle life.**
- **Prevent dendrite growth and limit "dead" Li formation.**

Any proposed future work is subject to change based on funding levels

Proposed Future Work for *FY 2020* and *FY2021*

▣ FY2020 Q3 Milestone:

Complete the investigation of radical disproportionation catalyst and test alternative electrolytes in which the solubility of polysulfide ions is lower than ether based electrolyte. .

▣ FY2020 Q4 Milestone:

Complete the initial design of the full cell consisting of polymeric sulfur compounds, alternative anode and adequate additive in either coin cell or pouch cell format.

FY2021 work:

- **Continue investigating the mechanism of sulfur redox reaction by in-situ techniques to monitoring both solid and liquid phases.**
- **Continue synthesizing new sulfur containing copolymer and inorganic anchor materials for performance (cycle life and energy density) improvement.**
- **Continue exploring alternative S electrode fabrication method to increase the loading of sulfur in engineered carbon structure and explore ways to produce thick sulfur cathode.**
- **Continue exploring alternative Li containing anode to alleviate “shuttle effect”.**
- **Continuing and enhancing the collaborative research with academic research institutions and industrial partners.**

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Summary

- Relevance
  - ✓ *Synthesis and test sulfur containing copolymers and composite to mitigate the migration of dissolved polysulfide ions.*
  - ✓ *Selection of alternative Li containing anode material to reduce the interaction between Li and dissolved polysulfides.*
  - ✓ *Optimization of the in-situ electrochemical techniques to further investigate the complex mechanism of sulfur cathode redox reaction in Li-S .*
- Approaches
  - ✓ *In-situ Electrochemical methods to investigate solid phase, liquid phase and interface. The overall electrochemical and chemical reactions of a Li-S battery can be monitored in real time.*
  - ✓ *Synthesis of polymer and inorganic sulfur composite materials to limit the dissolved polysulfide ion migration.*
  - ✓ *Dry method to make high aerial capacity electrodes.*
  - ✓ *Extended collaboration with other US and international academic institutions and US industrial partners.*
- Technical Accomplishments
  - ✓ *Li-S redox reaction mechanism became better understood through in-situ electrochemical studies.*
  - ✓ *Synthesized various polymeric and inorganic sulfur compounds with high loading, high rate and good cycle performance. The strong chemical bonding between host and sulfur can limit the dissolution of polysulfide.*
  - ✓ *Alternative Li-containing anode materials can significantly reduce the chemical interaction between the anode and dissolved polysulfide ions, which also can reduce the "shuttle-effect".*
- Proposed Future work
  - ✓ *Continue investigating the mechanism of sulfur redox reaction.*
  - ✓ *Continue synthesizing new sulfur containing copolymer and inorganic anchor materials for performance (cycle life and energy density) improvement.*
  - ✓ *Continue exploring alternative S electrode fabrication method to increase the loading of sulfur in engineered carbon structure and explore ways to produce thick sulfur cathode.*
  - ✓ *Continue exploring alternative Li-containing anode.*
  - ✓ *Continuing and enhancing the collaborative research with academic research institutions and industrial partners..*

Any proposed future work is subject to change based on funding levels